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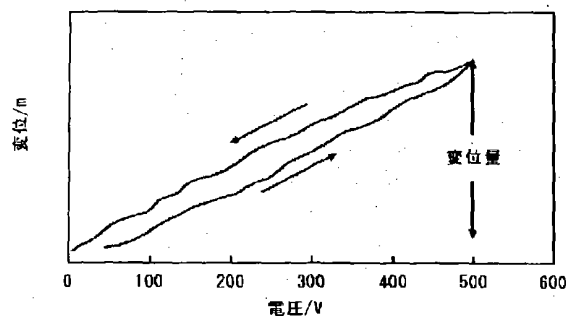
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(54) 【発明の名称】 圧電磁器組成物

(57) 【要約】

【課題】 特に高電界下での圧電変位量が大きく、かつ比誘電率の温度変化が小さいとともに、絶縁性に優れ、低温での焼結が可能な圧電磁器組成物を提供する。

【解決手段】 $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ で表記される 3 成分系ジルコンチタン酸鉛 (PZT) において、 $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ を 40 mol % 以下、 PbTiO_3 を 35 mol % 以上から 55 mol % 以下、 PbZrO_3 を 15 mol % 以上から 55 mol % 以下の範囲とし、前記 $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ の一部を $\text{Pb}(\text{B}_{11/2}\text{B}_{21/2})\text{O}_3$ で表され、その組成が、 $\text{B}_1 = \text{Ni}, \text{Zn}, \text{B}_2 = \text{W}, \text{Mo}$ の各々少なくとも 1 種類以上からなる組成物によって置換された組成で、分極軸と同一方向に、500 kV/m の直流電界を印加したときの圧電変位が、500 pm/V 以上を示し、かつ、 -40°C から 200°C の範囲で、比誘電率の温度変化が 300 % 以下とする圧電磁器組成物である。



【特許請求の範囲】

【請求項1】 $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ で表記される3成分系ジルコンチタン酸鉛(PZT)において、 $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ を40mol%以下、 PbTiO_3 を35mol%以上から55mol%以下の範囲、 PbZrO_3 を15mol%以上から55mol%以下の範囲とし、前記 $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ の一部を $\text{Pb}(\text{Bi}_{1/2}\text{B}_{21/2})\text{O}_3$ で表され、その組成が、 $\text{B}=\text{Ni}$ 、 Zn 、 $\text{B}_2=\text{W}$ 、 Mo の各々少なくとも1種類以上からなる組成物によって置換された組成で、分極軸と同一方向に、500kV/mの直流電界を印加したときの圧電変位が、500pm/V以上を示し、かつ、 -40°C から 200°C の範囲で、比誘電率の温度変化が300%以下であることを特徴とする圧電磁器組成物。

【請求項2】 請求項1記載の圧電磁器組成物が、その組成に関して、Nbを0mol%を超え2mol%以下の範囲で減量した組成であることを特徴とする圧電磁器組成物。

【請求項3】 請求項1または2のいずれかに記載の圧電磁器組成物の組成において、密度がピークを示す条件の焼成温度を、 $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ の3成分系ジルコンチタン酸鉛の母組成の焼結温度よりも低下させたことを特徴とする圧電磁器組成物。

【請求項4】 請求項1ないし3のいずれかに記載の圧電磁器組成物の組成において、Mnを MnO で表される酸化物に換算して、0wt%を超え0.10wt%以下の範囲で含有し、温度範囲 -40°C から 200°C における圧電磁器組成物の比抵抗が $1.0 \times 10^{11} \Omega \cdot \text{cm}$ 以上であることを特徴とする圧電磁器組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、ジルコンチタン酸鉛を主成分とする圧電磁器組成物に関するものであり、特に高電界下での圧電変位量が大きく、かつ、比誘電率の温度変化が小さいとともに、絶縁性に優れた圧電磁器組成物およびその製造方法に関するものである。

【0002】

【従来の技術】従来、圧電磁器材料としては、 PbTiO_3 や PbZrO_3 を主成分として含む圧電セラミックス(以下、PZT系圧電セラミックスと略す)や、複合ペロブスカイト類を第三、第四成分として固溶させた多成分系PZT系圧電セラミックスが、圧電定数が大であるために、圧電振動子を初めとしてアクチュエータ用の材料として広く利用されている。

【0003】これらの系の材料は、一般にモルフォトピック相境界(略称、MPB)近傍組成において、圧電定数(d定数)等の圧電変位に寄与する特性が向上するため、アクチュエータ用材料としては、前記のMPB近傍

組成の圧電磁器材料が広く実用化されている。

【0004】

【発明が解決しようとする課題】しかしながら、前記圧電定数は、一般に規格EMAS-6100等で示された共振-反共振法で求められた値であり、基本的には低電界(約数百V/m程度)印加時の圧電変位の割合を示している。これに対し、実際の圧電アクチュエータにおける駆動電界は、数百kV/mから数千kV/mにもなり、前記方法で求めた圧電定数が実用的な意味を持たない場合がある。

【0005】さらに、近年、圧電アクチュエータ利用範囲の広がりにともない、広い温度範囲での特性安定性、特に静電容量の温度安定性が求められている。例えば、自動車用部品として圧電アクチュエータが使用される場合には、その使用環境に応じて、 -40°C から 200°C にもなる広い温度範囲での特性安定性が要求される場合がある。

【0006】これに対し、一般に、前記MPB近傍組成での圧電磁器材料は、比誘電率の温度変動が大きくなり、広い温度範囲におけるアクチュエータ特性の安定性、特に静電容量の安定性に問題が生じている。

【0007】さらに、 $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ 系(以下、PNN-PZT系)の圧電磁器組成物は、d定数が大きいため、アクチュエータ素子用の圧電磁器材料として利用されている。しかし、圧電アクチュエータの応用範囲が広がるにつれ、さらに大きなd定数を持つ材料が求められている。

【0008】また、この系の圧電磁器材料は、電気抵抗率が比較的小さく、積層型圧電素子のように、一層の厚みが100μm前後の素子に使用した場合、印加できる電圧を大きくできず、十分な特性を引き出せなかったり、使用中に絶縁破壊してしまう等の問題点が生じている。また、前記PNN-PZT系圧電磁器材料は、電気抵抗率の温度変動も大きいため、特に前述のような広い温度範囲で使用する場合には、さらに信頼性が低下するなどの問題があった。

【0009】また、PNN-PZT系材料は、密度がピークを示す焼結温度が、同用途に用いられる $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ 系などの材料に比べ、 100°C 以上高く、積層型圧電素子に使用した場合、内部電極に高価なパラジウムを含むAg/Pd電極を用いる必要があり、コストの面で他材料より不利である。

【0010】従って、本発明の目的は、比誘電率の温度変動が小さく、アクチュエータ特性の温度依存性が安定している、コストが安い圧電磁器組成物を提供することである。

【0011】

【課題を解決するための手段】NiやZn、W、Moの酸化物の添加によって、圧電磁器組成物の低温での焼結

性が向上することは知られている。これらは、低融点の物質を添加することで、液相焼結の状態を作り、低温で緻密化を可能にするとされている。しかし、PNN-PZT系材料にW、Mo等の酸化物を単独添加した場合、試料の焼結性は大きく低下し、密度が低下したり、実用的な温度範囲では緻密化した試料は得られなかった。これは、イオンの電荷バランスを無視し、B2サイト原子が過剰となったためと考えられる。

【0012】本発明では、低温焼結化に有効な+6価の元素を単独ではなく+2価の元素と組み合わせることによって、ペロブスカイト ABO_3 のBサイトのイオンバランスを保持しつつ、焼結性改善を行えることを見出した。また、母成分のイオンバランスが保持されているため、添加物同士の相互干渉を気にすることなく添加物を追加して、さらに特性改善を進めることが可能であることを見出した。また、上記の圧電磁器材料に対して、Mnを含有することにより、表記の圧電磁器材料の絶縁性が向上することを見出した。

【0013】即ち、本発明は、 $PbTiO_3-PbZrO_3-Pb(Ni_{1/3}Nb_{2/3})O_3$ と表記される3成分系ジルコンチタン酸鉛(PZT)において、 $Pb(Ni_{1/3}Nb_{2/3})O_3$ を40mol%以下、 $PbTiO_3$ を35mol%以上から55mol%以下の範囲、 $PbZrO_3$ を15mol%以上から55mol%以下の範囲とし、前記 $Pb(Ni_{1/3}Nb_{2/3})O_3$ の一部を $Pb(B_{1/2}B_{2/2})O_3$ で表され、その組成が、 $B=Ni, Zn, B2=W, Mo$ の各々少なくとも1種類以上からなる組成物によって置換された組成で、分極軸と同一方向に、500kV/mの直流電界を印加したときの圧電変位が、500pC/V以上を示し、かつ、-40℃から200℃の範囲で、比誘電率の温度変化が300%以下とする圧電磁器組成物である。

【0014】また、本発明は、前記圧電磁器組成物が、その組成に関して、Nbを0mol%超え2mol%以下の範囲で減量した組成とする。

【0015】また、本発明は、前記圧電磁器組成物が、その組成に関して密度がピークを示す条件の焼成温度が $PbTiO_3-PbZrO_3-Pb(Ni_{1/3}Nb_{2/3})O_3$ の3成分系ジルコンチタン酸鉛の母組成の焼結温度よりも低下した圧電磁器組成物である。

【0016】また、本発明は、前記圧電磁器組成物の組成において、Mnを MnO で表される酸化物に換算して、0wt%を超え0.10wt%以下の範囲で含有し、-40℃から200℃における圧電磁器組成物の比抵抗が $1.0 \times 10^{11} \Omega \cdot cm$ 以上である圧電磁器組成物である。

【0017】

【発明の実施の形態】本発明の実施の形態による圧電磁器組成物について、以下に説明する。

【0018】本発明の圧電磁器組成物を以下の製造方法で作製した。即ち、酸化鉛(PbO)、酸化チタン(TiO_2)、酸化ジルコニウム(ZrO_2)、酸化ニッケル(NiO)、酸化ニオブ(Nb_2O_5)、酸化亜鉛(ZnO)、酸化タングステン(WO_3)、酸化モリブデン(MoO_3)、炭酸マンガンを($MnCO_3$)を原料として用い、目標組成となるように秤量し、これらの原料粉をジルコニアボールとともにアクリルボット中に入れ、20時間、湿式混合した。次に、これらの混合粉を脱水乾燥後、アルミナこう鉢中で予焼を行ってから、各予焼粉をアクリルボット中ジルコニアボールにて15時間、湿式粉砕した。

【0019】引き続き、脱水乾燥して得られた予焼粉砕粉にバインダを混合して加圧し、 $\phi 20 \times T 3mm$ に成形した。この成形体を900~1260℃で2時間焼成し、各焼結体を1mmの厚さに加工した後、両面に銀ペーストを塗布して450℃で焼き付けて電極を形成することにより、それぞれ組成の異なる評価用の試料とした。

【0020】このようにして得られた各試料を2kV/mmで分極処理し、インピーダンスアナライザ(HP4194A)と恒温槽を使用して、1kHzの比誘電率 ϵ_r の温度特性を測定した。温度特性は、-40℃から400℃の範囲で5℃から10℃毎に30分保持したのち、各温度での1kHzの比誘電率 ϵ_r を測定した。

【0021】また、 d_{33} (500kV)は、2mm ϕ の円柱で、上下方向から試料の中心領域にて支持した状態で、前記試料に、2秒間で等速にて、0V→500V→0Vの電圧を印加し、試料厚さ方向の変位をフリンジカウンタ式レーザ変位計を使用して測定して算出した。

【0022】図1に、 d_{33} (500kV)の測定例を示す。図1に示すように、厚さ1mmの測定試料に、500Vの直流電圧印加時(電界強度500kV/m)の変位量から d_{33} (500kV)を算出した。

【0023】

【実施例】本発明の実施例による圧電磁器組成物について、以下に説明する。

【0024】(実施例1)本発明の実施例1による圧電磁器組成物およびその製造方法について説明する。表1に、組成物の焼成密度がピークを示す温度と、 d_{33} (500kV)と、-40℃から200℃の範囲での ϵ_r の温度変化率を示す。表1中、*のついた試料No.は、本発明の比較例の圧電磁器組成物を示しており、*のない試料No.が、本発明の実施例による圧電磁器組成物を示している。また、置換する成分は、B1元素とB2元素、置換量を並べて表記している。

【0025】

【表1】

	試料No.	第3成分	PbTiO ₃	PbZrO ₃	第3成分置換	添加	減量	焼結ピーク 温度	d ₃₃ (500kV) /pm·V ⁻¹	温度範囲 -40~+200℃ Δεr/%
*	1	35	50	15	—	—	—	1230	450	230
*	2	35	40	25	—	—	—	1230	1000	210
*	3	35	35	30	—	—	—	1230	800	280
*	4	10	55	35	—	—	—	1260以上	470	155
*	5	5	40	55	—	—	—	1260以上	400	280
	6	35	50	15	ZnW5mol%	—	—	1140	530	200
	7	10	55	35	ZnW1.5mol%	—	—	1200	520	150
	8	5	40	55	ZnW1.5mol%	—	—	1200	500	260
*	9	30	39.5	30.5	—	—	—	1170	720	210
*	10	30	39.5	30.5	—	W0.75mol%	—	1200	750	190
*	11	30	39.5	30.5	—	W1.5mol%	—	1200	700	200
*	12	25	41.5	33.5	—	—	—	1200	825	165
*	13	25	41.5	33.5	—	Mn0.005wt%	—	1200	935	163
*	14	25	41.5	33.5	Ni0.5mol%	Mn0.005wt%	—	1170	840	181
*	15	25	41.5	33.5	Ni1.0mol%	Mn0.005wt%	—	1140	560	184
*	16	25	41.5	33.5	Ni3.0mol%	Mn0.005wt%	—	1140	310	176
*	17	25	41.5	33.5	Nb0.5mol%	Mn0.005wt%	—	1200	780	190
*	18	25	41.5	33.5	Nb1mol%	Mn0.005wt%	—	1230	670	215
*	19	25	41.5	33.5	Nb3mol%	Mn0.005wt%	—	1260以上	*	*
*	20	25	41.5	33.5	Mo0.5mol%	Mn0.005wt%	—	1230	540	170
*	21	25	41.5	33.5	Mo1mol%	Mn0.005wt%	—	1260以上	560	183
*	22	25	41.5	33.5	Mo3mol%	Mn0.005wt%	—	1260以上	680	200
	23	25	41.5	33.5	NiW2mol%	Mn0.005wt%	—	1200	1050	168
	24	25	41.5	33.5	NiW5mol%	Mn0.005wt%	—	1170	925	172
	25	25	41.5	33.5	NiW2mol%	Mn0.005wt%	Nb0.33mol%	1170	889	185
	26	25	41.5	33.5	ZnW2mol%	Mn0.005wt%	—	1170	960	175
	27	25	41.5	33.5	ZnW5mol%	Mn0.005wt%	—	1100	915	165
	28	25	41.5	33.5	ZnW2mol%	Mn0.005wt%	Nb0.33mol%	1140	890	167
	29	25	41.5	33.5	ZnW5mol%	Mn0.005wt%	Nb0.50mol%	1100	1000	170
	30	25	41.5	33.5	ZnW5mol%	Mn0.005wt%	Nb1.00mol%	950	1130	175
*	31	12	44.5	43.5	—	Mn0.005wt%	—	1280以上	350	143
*	32	12	44.5	43.5	ZnNb1.5mol%	Mn0.005wt%	—	1260以上	480	164
	33	12	44.5	43.5	ZnW1.5mol%	Mn0.005wt%	—	1230	520	161
	34	12	44.5	43.5	ZnW1.5mol% NiW0.25mol%	Mn0.005wt% Nb0.25mol%	—	1230	785	162
	35	12	44.5	43.5	ZnW1.5mol% NiW0.5mol%	Mn0.005wt% Nb0.50mol%	—	1170	890	157
	36	12	44.5	43.5	ZnW3.0mol%	Mn0.005wt%	—	1200	630	166
	37	12	44.5	43.5	ZnW3.0mol%	Mn0.005wt%	Nb1.00mol%	1000	925	160
	38	12	44.5	43.5	ZnW4.5mol%	Mn0.005wt%	—	1170	600	159
	39	12	44.5	43.5	ZnW4.5mol%	Mn0.005wt%	Nb1.00mol%	950	955	180
	40	12	44.5	43.5	ZnW4.5mol%	Mn0.005wt%	Nb0.50mol%	1000	980	172
	41	12	44.5	43.5	NiW3.0mol%	Mn0.005wt%	—	1170	720	155
	42	12	44.5	43.5	NiW3.0mol%	Mn0.005wt%	Nb1.00mol%	1050	680	158
	43	12	44.5	43.5	NiW4.5mol%	Mn0.005wt%	—	1200	650	150
	44	12	44.5	43.5	NiW4.6mol%	Mn0.005wt%	Nb1.00mol%	1000	790	162
	45	12	44.5	43.5	NiW4.5mol%	Mn0.005wt%	Nb0.50mol%	1050	890	159

(注) *印は、比較例を示す

【0026】母成分である試料9に対し、Wを添加した試料10、試料11、また母成分試料12を基本とした試料13にMoを置換した試料20～試料22らは、共に焼結性が下がり、緻密化ピーク温度が上昇している。これは、+6価のイオンが入ったことで、B2サイトが過剰になり、Nbを増量した試料17～試料19と同様の効果が現れていると考えられる。

【0027】それに対し、試料12を基本とした試料13に+2価のNiイオンが置換された試料14～試料16では、焼結性は改善されるが、添加量と共にd₃₃ (500kV) が低下してゆく。このように、電荷バランスを考慮しない添加方法では、添加量が増加すると母成分の材料特性が劣化し、意図する特性が得られなくなってしまう。

【0028】本発明による試料について説明する。試料13に対し、NiとWの組み合わせで置換した試料23、試料24では、焼結性の向上を原因とするd₃₃ (500kV) の増加、焼結温度の低下が認められる。同様に、ZnとWの組み合わせで置換した試料26、試料27では、焼結温度の低下が著しく、NiWよりも高い効果が得られている。また、試料31を母成分とした試料33、試料36、試料38、試料41、試料43でも同様の効果が得られている。

【0029】ここで、本請求項での範囲の限定の根拠について言及する。第三成分が40mol%を超えた場合、その化合物のキュリー温度T_cは低下し、目的の温度範囲での使用が困難になるため、請求範囲から除外する。また、ε_rの温度変化率は、MPB近辺およびZr

成分が少ない範囲では目標に合致するものが得られるが、MPB近傍よりZr成分が多い範囲では、変化率が大きく、目的とする性能が得られなかった。本発明では、Ti成分が35mol%未満の範囲では目的に合わないため、請求項の範囲から除外した。

【0030】また、試料1にZnとWの組み合わせで置換した試料6において、 d_{33} (500kV) がほぼ目的の最小値を示したため、Zr成分の最小範囲を15mol%まで、同じく試料4にZnとWの組み合わせで置換した試料7において、 d_{33} (500kV) がほぼ目的の最小値を示したため、Ti成分の最大範囲を55mol%まで、同じく試料5にZnとWの組み合わせで置換した試料8において、 d_{33} (500kV) が目的の最小値を示したため、Zr成分の最大範囲を55mol%までとした。

【0031】(実施例2) 本発明の実施例2による圧電磁器組成物について説明する。実施例1により作製された試料23に対し、Nb量を減少させた試料25、試料26に対する試料28、試料27に対する試料30および31、試料36に対する試料37、試料38に対する試料39および試料40、試料41に対する試料42、試料43に対する試料44および試料45では、焼結密度ピーク温度が低下している。

【0032】Nb量が少ない試料27に対する試料29の場合も、焼結密度ピーク温度は変わらないように見えるが、焼結性の向上により d_{33} (500kV) の向上が認められる。ここで、Nbの減量が2mol%を超える場合、電荷バランスが多く崩れすぎて、絶縁抵抗値が大きく劣化するため、これ以上のNbの減量は範囲外とした。

【0033】(実施例3) 本発明の実施例3による圧電磁器組成物について説明する。酸化鉛(PbO)、酸化

チタン(TiO_2)、酸化ジルコニウム(ZrO_2)、酸化ニッケル(NiO)、酸化ニオブ(Nb_2O_5)、酸化亜鉛(ZnO)、酸化タングステン(WO_3)、酸化モリブデン(MoO_3)、炭酸マンガンを(MnCO_3)を原料として用い、目的組成となるように秤量し、実施例1と同様に、試料を作製、 -40°C および 200°C において、それぞれでの比抵抗を測定した。

【0034】その結果の一例を図2に示す。図2より、高温領域では比抵抗が低下するものの、 MnO_3 を極微量添加するだけで、比抵抗が顕著に向上し、本発明の目標値を満足することがわかる。また、 MnO の添加量は、0.05wt%を超えると、それ以上の比抵抗向上効果は望め無いがわかった。また、 MnO の過剰な添加は、圧電定数などの圧電特性を劣化させる傾向もあるが、母成分の比抵抗が低い材料の場合、 MnO の添加量が0.05wt%の場合、特性的には十分であるが、特性の安定する0.10wt%まで添加することが望ましい。よって、0.10wt%以下が、本発明の目標に対して適当な値であると判断できる。

【0035】

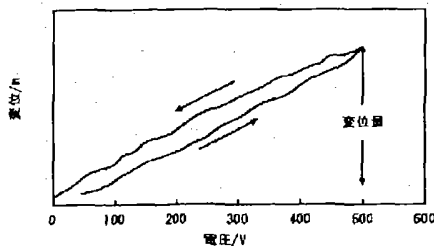
【発明の効果】以上、説明したように、本発明によれば、高電圧印加時の圧電歪定数が大きく、かつ、比誘電率の温度変化が小さく、高温温度範囲での電気抵抗率も大きく、広い温度範囲で安定な特性を有する、低温焼結が可能な、低コストなアクチュエータ用材料として極めて有用な圧電磁器組成物を提供できるものである。

【図面の簡単な説明】

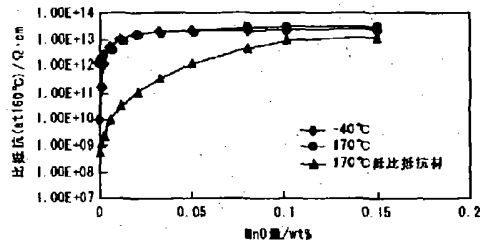
【図1】本発明による実施例1の圧電磁器組成物について、圧電定数 d_{33} (500kV) 測定方法によって得られる印加電圧と圧電変位の関係を示す図。

【図2】本発明による実施例3の圧電磁器組成物で示したMnO添加量と比抵抗の関係を示す図。

【図1】



【図2】



Application Number: JP20010021971 20010130
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EC Classification:
Equivalents:

SOLUTION: The piezoelectric ceramic composition is that, in a three component system lead zirconate titanate (PZT) represented by $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ a content of $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ is ≤ 40 mol%, that of PbTiO_3 is ≥ 35 mol% and ≤ 55 mol%, that of PbZrO_3 is ≥ 15 mol% and ≤ 55 mol%, and a part of $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ is represented by $\text{Pb}(\text{B}_{11/2}\text{B}_{21/2})\text{O}_3$, the composition of which is represented by a composition each of which is substituted by at least one or more kinds of $\text{B}_1=\text{Ni, Zn, B}_2=\text{W, Mo}$. The piezoelectric displacement in case of impressing D.C. electric field intensity of 500 kV/m in the same direction with a polarization axis shows ≥ 500 pm/V, and the temperature change of the dielectric constant over the range from -40 deg.C to 200 deg.C is $\leq 300\%$.

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CLAIMS

[Claim(s)]

[Claim 1] In 3 component system zircon lead titanate (PZT) written by $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{nickel}_{1/3}\text{Nb}_{2/3})\text{O}_3$ Less than [40mol%] and PbTiO_3 for $\text{Pb}(\text{nickel}_{1/3}\text{Nb}_{2/3})\text{O}_3$ The range not more than [more than 35mol% to] 55mol%, PbZrO_3 is made into the range not more than 55mol% more than from 15mol%. a part of aforementioned $\text{Pb}(\text{nickel}_{1/3}\text{Nb}_{2/3})\text{O}_3$ are expressed with $\text{Pb}(\text{B}_{11}\text{-}/2\text{B}_s\text{ }21/2)\text{O}_3$ -- having -- the composition -- B= 1 -- nickel, Zn, and B-2= -- each of W and Mo -- by the composition replaced with the constituent which consists of one or more kinds even if few the piezo-electricity when impressing the direct-current electric field of 500 kV/m in the same direction as a polarization shaft -- the piezoelectric-ceramics constituent which a variation rate shows 500 or more pm/V, and is characterized by the temperature change of specific inductive capacity being 300% or less in -40 to 200 degrees C

[Claim 2] The piezoelectric-ceramics constituent characterized by a piezoelectric-ceramics constituent according to claim 1 being the composition which exceeded zero-mol% for Nb about the composition, and reduced its weight in not more than 2mol%.

[Claim 3] The piezoelectric-ceramics constituent with which density is characterized by making it fall rather than the sintering temperature of mother composition of the burning temperature of the conditions which show a peak of 3 component system zircon lead titanate of $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{nickel}_{1/3}\text{Nb}_{2/3})\text{O}_3$ in composition of a piezoelectric-ceramics constituent given in either of the claims 1 or 2.

[Claim 4] The piezoelectric-ceramics constituent which converts Mn into the oxide expressed with MnO in composition of a piezoelectric-ceramics constituent according to claim 1 to 3, exceeds 0wt%, contains in not more than 0.10wt%, and is characterized by the specific resistance of the piezoelectric-ceramics constituent in 200 degrees C being 1.0×10^{11} or more ohm-cm from -40 degrees C of temperature requirements.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] the thing about the piezoelectric-ceramics constituent with which this invention makes a zircon lead titanate a principal component -- it is -- especially -- the piezo-electricity under high electric field -- a variation rate -- while an amount is large and the temperature change of specific inductive capacity is small, it is related with the piezoelectric-ceramics constituent excellent in insulation, and its manufacture method

[0002]

[Description of the Prior Art] Conventionally, as a piezoelectric-ceramics material, since a piezoelectric constant is size, the electrostrictive ceramics (it abbreviates to PZT system electrostrictive ceramics hereafter) which contains PbTiO_3 and PbZrO_3 as a principal component, and the multicomponent system PZT system electrostrictive ceramics which made compound perovskites dissolve as the third fourth component are widely used as a material for actuators by making a piezoelectric transducer into the start.

[0003] the material of these systems -- general -- composition near the mol photograph pick phase boundary (an abbreviated name, MPB) -- setting -- piezo-electricity, such as a piezoelectric constant (d constant), -- since the property which contributes to a variation rate improves, as a charge of actuator material, piezoelectric-ceramics material of the aforementioned composition near the MPB is put in practical use widely

[0004]

[Problem(s) to be Solved by the Invention] however, the value calculated by the resonance-antiresonating method by which the aforementioned piezoelectric constant was generally shown in the specification EMAS-6100 grade -- it is -- fundamental -- the piezo-electricity at the time of low electric-field (about 100 V/m of divisors) impression -- the rate of a variation rate is shown On the other hand, the drive electric field in an actual electrostrictive actuator may also become number 1000 kV/m from hundreds kV/m, and may not have a meaning with the practical piezoelectric constant for which it asked by the aforementioned method.

[0005] Furthermore, in connection with the breadth of the electrostrictive actuator use range, the property stability in a latus temperature requirement, especially the temperature stability of electrostatic capacity are called for in recent years. For example, when an electrostrictive actuator is used as parts for automobiles, according to the operating environment, the property stability in the latus temperature requirement which becomes no less than 200 degrees C from -40 degrees C may be required.

[0006] On the other hand, generally, temperature change of specific inductive capacity became large, and the problem has produced the piezoelectric-ceramics material in the aforementioned composition near the MPB at the stability of the actuator property in a latus temperature requirement, especially the stability of electrostatic capacity.

[0007] Furthermore, since d constant is large, the piezoelectric-ceramics constituent of PbTiO_3 - PbZrO_3 - $\text{Pb}(\text{nickel}_{1/3}\text{Nb}_{2/3})\text{O}_3$ system (henceforth, PNN-PZT system) is used as a piezoelectric-ceramics

material for AKUYUETA elements. However, material with still bigger d constant is called for as the application range of an electrostrictive actuator spreads.

[0008] Moreover, the piezoelectric-ceramics material of this system has comparatively small electrical resistivity, like a laminating type piezoelectric device, when much more thickness uses it for the element around 100 micrometers, voltage which can be impressed could not be enlarged, but sufficient property cannot be pulled out or the trouble of carrying out dielectric breakdown during use has produced it.

Moreover, since the temperature change of electrical resistivity of the aforementioned PNN-PZT system piezoelectric-ceramics material was also large, when using it by the above large temperature requirements especially, it had the problem of reliability falling further.

[0009] Moreover, the sintering temperature density indicates a peak to be is high 100 degrees C or more compared with material, such as $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ system used for this use, when it is used for a laminating type piezoelectric device, the Ag/Pd electrode which contains expensive palladium in an internal electrode needs to be used for PNN-PZT system material, and it is more disadvantageous than other material in respect of cost.

[0010] Therefore, the purpose of this invention has a small temperature change of specific inductive capacity, and it is offering the piezoelectric-ceramics constituent with cheap cost whose temperature dependence of an actuator property is stable.

[0011]

[Means for Solving the Problem] It is known by addition of nickel or the oxide of Zn, W, and Mo that the degree of sintering in the low temperature of a piezoelectric-ceramics constituent will improve. These are adding the matter of the low melting point, make the state of liquid phase sintering and are supposed that precise-ization is enabled at low temperature. However, when independent addition of the oxides, such as W and Mo, was carried out at PNN-PZT system material, the degree of sintering of a sample fell greatly, density did not fall and the sample which turned precisely was not obtained in a practical temperature requirement. This disregards the charge balance of ion and is considered because B-2 site atom became superfluous.

[0012] In this invention, it found out that a degree-of-sintering improvement could be made, holding the ion balance of B site of a perovskite ABO_3 by combining the element of +6 ** effective in low-temperature-sintering-izing with a + divalent element rather than being independent. Moreover, since the ion balance of a mother component was held, it found out that it was possible to add an additive, without caring about the mutual interference of additives, and to advance a property improvement further. Moreover, it found out that the insulation of a declared piezoelectric-ceramics material improved by containing Mn to the above-mentioned piezoelectric-ceramics material.

[0013] Namely, this invention is set to 3 component system zircon lead titanate (PZT) it writes $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{nickel}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [lead titanate]. Less than [40mol%] and PbTiO_3 for $\text{Pb}(\text{nickel}_{1/3}\text{Nb}_{2/3})\text{O}_3$ The range not more than [more than 35mol% to] 55mol%, PbZrO_3 is made into the range not more than 55mol% more than from 15mol%. It is expressed with $\text{Pb}(\text{B}_{11-2}\text{B}_{21/2})\text{O}_3$, and the composition a part of aforementioned $\text{Pb}(\text{nickel}_{1/3}\text{Nb}_{2/3})\text{O}_3$ by the composition replaced with the constituent of B=nickel, Zn, B-2=W, and Mo which consists of at least one or more kinds respectively the piezo-electricity when impressing the direct-current electric field of 500 kV/m in the same direction as a polarization shaft -- a variation rate shows 500 or more pm/V, and the range of it is -40 to 200 degrees C, and it is the piezoelectric-ceramics constituent which the temperature change of specific inductive capacity makes 300% or less

[0014] moreover, this invention -- the aforementioned piezoelectric-ceramics constituent -- the composition -- being related -- Nb -- zero-mol% -- it considers as the composition exceeded and the quantity of was decreased in not more than 2mol%

[0015] Moreover, the aforementioned piezoelectric-ceramics constituent of this invention is a piezoelectric-ceramics constituent with which density fell about the composition rather than the sintering temperature of mother composition of the burning temperature of the conditions which show a peak of 3 component system zircon lead titanate of $\text{PbTiO}_3\text{-PbZrO}_3\text{-Pb}(\text{nickel}_{1/3}\text{Nb}_{2/3})\text{O}_3$.

[0016] Moreover, in composition of the aforementioned piezoelectric-ceramics constituent, this

invention converts Mn into the oxide expressed with MnO, exceeds 0wt%, contains it in not more than 0.10wt%, and is a piezoelectric-ceramics constituent whose specific resistance of the piezoelectric-ceramics constituent in -40 degrees C to 200 degrees C is 1.0×10^{11} or more ohm-cm.

[0017]

[Embodiments of the Invention] The piezoelectric-ceramics constituent by the gestalt of operation of this invention is explained below.

[0018] The piezoelectric-ceramics constituent of this invention was produced by the following manufacture methods. Namely, using a lead oxide (PbO), titanium oxide (TiO₂), a zirconium oxide (ZrO₂), nickel oxide (NiO), a niobium oxide (Nb₂O₅), a zinc oxide (ZnO), a tungstic oxide (WO₃), a molybdenum oxide (MoO₃), and manganese carbonate (MnCO₃) as a raw material, weighing capacity was carried out so that it might become a target system, and such raw material powder was put in into the acrylic pot with the zirconia ball, and carried out wet blending for 20 hours. Next, after performing **** for these mixed powder in alumina ***** after dehydration dryness, wet grinding of each ***** was carried out with the zirconia ball in an acrylic pot for 15 hours.

[0019] Then, the binder was mixed to the **** pulverized powder obtained by carrying out dehydration dryness, it was pressurized, and it fabricated to $\phi 20 \times T3 \text{mm}$. After calcinating this Plastic solid at 900-1260 degrees C for 2 hours and processing each sintered compact into the thickness of 1mm, it considered as the sample for evaluation from which composition differs, respectively by applying a silver paste to both sides, printing at 450 degrees C, and forming an electrode.

[0020] Thus, polarization processing of each obtained sample was carried out by mm in 2kV /, the impedance analyzer (H.P.4194A) and the thermostat were used, and the 1kHz temperature characteristic of specific-inductive-capacity ϵ_{r} was measured. After holding the temperature characteristic every 10 degrees C from 5 degrees C in -40 to 400 degrees C for 30 minutes, it measured specific-inductive-capacity [of 1kHz] ϵ_{r} in each temperature.

[0021] Moreover, it is the pillar of 2mmphi, and d33 (500kV) was in the state supported in the central field of a sample from the upper and lower sides, in 2 seconds, at uniform velocity, it impressed the voltage of 0V ->500V ->0V, and measured and computed the variation rate of the sample thickness direction in the aforementioned sample using the fringe counter formula laser displacement gage.

[0022] The example of measurement of d33 (500kV) is shown in drawing 1. it is shown in drawing 1 -- as -- a measurement sample with a thickness of 1mm -- the variation rate at the time of direct-current-voltage impression of 500V (field strength 500 kV/m) -- d33 (500kV) was computed from the amount

[0023]

[Example] The piezoelectric-ceramics constituent by the example of this invention is explained below.

[0024] (Example 1) The piezoelectric-ceramics constituent by the example 1 and its manufacture method of this invention are explained. The baking density of a constituent indicates the rates of a temperature change of ϵ_{r} in the range of -40 to 200 degrees C to be the temperature which shows a peak, and d33 (500kV) to Table 1. Among Table 1, sample No. which * attached shows the piezoelectric-ceramics constituent of the example of comparison of this invention, and sample No. without * shows the piezoelectric-ceramics constituent by the example of this invention. Moreover, the component to replace has put in order and written B1 element, B-2 element, and the amount of substitution.

[0025]

[Table 1]

試料No.	第3成分	PbTiO ₃	PbZrO ₃	第3成分置換	添加	減量	焼結ピーク 温度	d ₃₃ (500kV) /pm·V ⁻¹	温度範囲 -40~+200℃ Δε _r /%
1	35	50	15	—	—	—	1230	450	230
2	35	40	25	—	—	—	1230	1000	210
3	35	35	30	—	—	—	1230	800	280
4	10	55	35	—	—	—	1260以上	470	155
5	5	40	55	—	—	—	1260以上	400	280
6	35	50	15	ZnW5mol%	—	—	1140	530	200
7	10	55	35	ZnW1.5mol%	—	—	1200	520	150
8	5	40	55	ZnW1.5mol%	—	—	1200	500	260
9	30	39.5	30.5	—	—	—	1170	720	210
10	30	39.5	30.5	—	W0.75mol%	—	1200	750	190
11	30	39.5	30.5	—	W1.5mol%	—	1200	700	200
12	25	41.5	33.5	—	—	—	1200	825	165
13	25	41.5	33.5	—	Mn0.005wt%	—	1200	935	163
14	25	41.5	33.5	Ni0.5mol%	Mn0.005wt%	—	1170	840	161
15	25	41.5	33.5	Ni1.0mol%	Mn0.005wt%	—	1140	560	184
16	25	41.5	33.5	Ni3.0mol%	Mn0.005wt%	—	1140	310	176
17	25	41.5	33.5	Nb0.5mol%	Mn0.005wt%	—	1200	780	180
18	25	41.5	33.5	Nb1mol%	Mn0.005wt%	—	1230	670	215
19	25	41.5	33.5	Nb3mol%	Mn0.005wt%	—	1260以上	*	*
20	25	41.5	33.5	Mo0.5mol%	Mn0.005wt%	—	1230	540	170
21	25	41.5	33.5	Mo1mol%	Mn0.005wt%	—	1260以上	560	183
22	25	41.5	33.5	Mo3mol%	Mn0.005wt%	—	1260以上	660	200
23	25	41.5	33.5	NiW2mol%	Mn0.005wt%	—	1200	1050	166
24	25	41.5	33.5	NiW5mol%	Mn0.005wt%	—	1170	925	172
25	25	41.5	33.5	NiW2mol%	Mn0.005wt%	Nb0.33mol%	1170	888	185
26	25	41.5	33.5	ZnW2mol%	Mn0.005wt%	—	1170	960	175
27	25	41.5	33.5	ZnW5mol%	Mn0.005wt%	—	1100	915	165
28	25	41.5	33.5	ZnW2mol%	Mn0.005wt%	Nb0.33mol%	1140	890	167
29	25	41.5	33.5	ZnW5mol%	Mn0.005wt%	Nb0.50mol%	1100	1000	170
30	25	41.5	33.5	ZnW5mol%	Mn0.005wt%	Nb1.00mol%	950	1130	175
31	12	44.5	43.5	—	Mn0.005wt%	—	1260以上	350	143
32	12	44.5	43.5	ZnNb1.5mol%	Mn0.005wt%	—	1260以上	480	164
33	12	44.5	43.5	ZnW1.5mol%	Mn0.005wt%	—	1230	520	161
34	12	44.5	43.5	NiW0.25mol%	Mn0.005wt%	Nb0.25mol%	1230	785	162
35	12	44.5	43.5	NiW0.5mol%	Mn0.005wt%	Nb0.50mol%	1170	890	157
36	12	44.5	43.5	ZnW3.0mol%	Mn0.005wt%	—	1200	630	166
37	12	44.5	43.5	ZnW3.0mol%	Mn0.005wt%	Nb1.00mol%	1000	825	160
38	12	44.5	43.5	ZnW4.5mol%	Mn0.005wt%	—	1170	600	159
39	12	44.5	43.5	ZnW4.5mol%	Mn0.005wt%	Nb1.00mol%	950	955	180
40	12	44.5	43.5	ZnW4.5mol%	Mn0.005wt%	Nb0.50mol%	1000	980	172
41	12	44.5	43.5	NiW3.0mol%	Mn0.005wt%	—	1170	720	155
42	12	44.5	43.5	NiW3.0mol%	Mn0.005wt%	Nb1.00mol%	1050	680	159
43	12	44.5	43.5	NiW4.5mol%	Mn0.005wt%	—	1200	650	150
44	12	44.5	43.5	NiW4.5mol%	Mn0.005wt%	Nb1.00mol%	1000	790	162
45	12	44.5	43.5	NiW4.5mol%	Mn0.005wt%	Nb0.50mol%	1050	890	159

(注) *印は、比較例を示す

[0026] To the sample 9 which is a mother component, a degree of sintering falls and, as for sample 20 - sample 12 and others both which replaced Mo by the sample 10 which added W, the sample 11, and the sample 13 based on the mother component sample 12, precise-ized peak temperature is rising. This is that the ion of +6 ** entered, and B-2 site becomes superfluous and it is considered that the same effect as the sample 17 which increased the quantity of Nb - a sample 19 has shown up.

[0027] By the sample 14 - sample 16 by which + divalent nickel ion was replaced by the sample 13 based on a sample 12 to it, although a degree of sintering improves, d₃₃ (500kV) falls with an addition. Thus, by the addition method of not taking charge balance into consideration, if an addition increases, the material property of a mother component will deteriorate and the property to mean will no longer be acquired.

[0028] The sample by this invention is explained. By the sample 23 replaced in the combination of

nickel and W, and the sample 24, the increase in d33 (500kV) which considers improvement in a degree of sintering as a cause, and the fall of sintering temperature are accepted to a sample 13. Similarly, by the sample 26 and sample 27 which were replaced in the combination of Zn and W, the fall of sintering temperature is remarkable and the effect higher than NiW is acquired. Moreover, the effect with the same said also of the sample 33 which used the sample 31 as the mother component, a sample 36, a sample 38, a sample 41, and a sample 43 is acquired.

[0029] Here, reference is made about the basis of limitation of the range of this claim. When the third component exceeds 40-mol%, since it falls and use by the target temperature requirement becomes difficult, Curie-temperature T_c of the compound is excepted from a generic claim. Moreover, although that with which the MPB neighborhood and Zr component agree at a target in the few range was obtained, in the range with many Zr components near the MPB, rate of change was large and, as for the rate of a temperature change of ϵ_{r} , the target performance was not obtained. In this invention, since Ti component did not suit the purpose in below 35mol%, it excepted from the range of a claim.

[0030] Since d33 (500kV) showed the target minimum value mostly, in the sample 6 replaced by the sample 1 in the combination of Zn and W, the minimum range of Zr component moreover, to 15-mol% Since d33 (500kV) showed the target minimum value mostly, in the sample 7 similarly replaced by the sample 4 in the combination of Zn and W, the maximum range of Ti component to 55-mol% In the sample 8 similarly replaced by the sample 5 in the combination of Zn and W, since d33 (500kV) showed the target minimum value, the maximum range of Zr component was carried out to to 55-mol%.

[0031] (Example 2) The piezoelectric-ceramics constituent by the example 2 of this invention is explained. By the sample 44 and sample 45 to the sample 42 and sample 43 to the sample 39 to the sample 37 and sample 38 to the samples 30 and 31 and sample 36 to the sample 28 and sample 27 to the sample 25 and sample 26 which decreased the amount of Nb(s) and a sample 40, and a sample 41, sintered density peak temperature is falling to the sample 23 produced by the example 1.

[0032] Although sintered density peak temperature seems not to change also in the sample 29 to the sample 27 with few amounts of Nb(s), improvement in d33 (500kV) is accepted by improvement in a degree of sintering. Here, since charge balance collapsed too much mostly and insulating resistance deteriorated greatly when loss in quantity of Nb exceeds two-mol%, loss in quantity of Nb beyond this presupposed that it is out of range.

[0033] (Example 3) The piezoelectric-ceramics constituent by the example 3 of this invention is explained. Using a lead oxide (PbO), titanium oxide (TiO₂), a zirconium oxide (ZrO₂), nickel oxide (NiO), a niobium oxide (Nb₂O₅), a zinc oxide (ZnO), a tungstic oxide (WO₃), a molybdenum oxide (MoO₃), and manganese carbonate (MnCO₃) as a raw material, weighing capacity was carried out so that it might become the purpose composition, and the specific resistance which comes out of a sample in production, -40 degrees C, and 200 degrees C, respectively was measured like the example

[0034] An example of the result is shown in drawing 2. In an elevated-temperature field, drawing 2 shows that specific resistance improves notably and is satisfied [only with carrying out ultralow-volume addition of MnO₃] of the desired value of this invention, although specific resistance falls. Moreover, when the addition of MnO exceeded 0.05wt%, it turns out that the improvement effect in specific resistance beyond it can be desired, and there is nothing. Moreover, although superfluous addition of MnO is enough in property when the specific resistance of a mother component is low material and the addition of MnO is 0.05wt(s)%, although it tends to degrade piezo-electric properties, such as a piezoelectric constant, adding to 0.10wt(s)% by which a property is stabilized is desirable. Therefore, less than [0.10wt%] can judge that it is a suitable value to the target of this invention.

[0035]

[Effect of the Invention] As mentioned above, as explained, according to this invention, a piezoelectric-ceramics constituent the temperature change of specific inductive capacity is small, large [the piezo-electric distorted constant at the time of high-voltage impression is large, and] the electrical resistivity in the high temperature range and very useful as a low cost charge of actuator material which has a stable property by the latus temperature requirement and in which low temperature sintering is possible can be offered.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] Conventionally, as a piezoelectric-ceramics material, since a piezoelectric constant is size, the electrostrictive ceramics (it abbreviates to PZT system electrostrictive ceramics hereafter) which contains PbTiO_3 and PbZrO_3 as a principal component, and the multicomponent system PZT system electrostrictive ceramics which made compound perovskites dissolve as the third fourth component are widely used as a material for actuators by making a piezoelectric transducer into the start.

[0003] the material of these systems -- general -- composition near the mol photograph pick phase boundary (an abbreviated name, MPB) -- setting -- piezo-electricity, such as a piezoelectric constant (d constant), -- since the property which contributes to a variation rate improves, as a charge of actuator material, piezoelectric-ceramics material of the aforementioned composition near the MPB is put in practical use widely

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing showing the relation of the piezo-electric displacement by the applied voltage obtained by piezoelectric-constant d33 (500kV) measuring method about the piezoelectric-ceramics constituent of the example 1 by this invention.

[Drawing 2] Drawing showing the relation of the MnO addition and specific resistance which were shown with the piezoelectric-ceramics constituent of the example 3 by this invention.

[Translation done.]

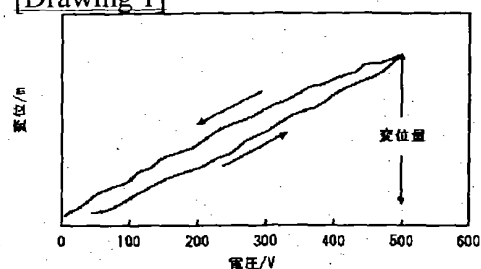
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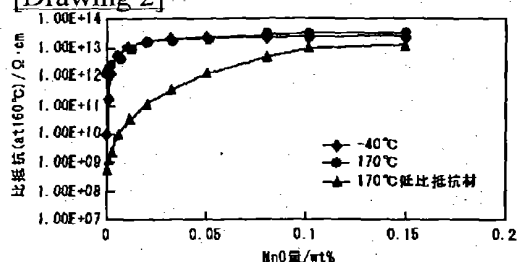
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DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]